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CITATION:

Ito, Setsuro ...[et al]. Formation of Stable  $\gamma$ -6BiO • SiO Crystal from Its Supercooled Melt and Metastable Crystal Induced by Their Surface-Contamination. Bulletin of the Institute for Chemical Research, Kyoto University 1978, 56(5): 286-295

ISSUE DATE:

1978-12-20

URL:

<http://hdl.handle.net/2433/76788>

RIGHT:

## Formation of Stable $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ Crystal from Its Supercooled Melt and Metastable Crystal Induced by Their Surface-Contamination

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*Received September 20, 1978*

A  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt, when naturally cooled in a platinum crucible to room temperature, precipitated only the metastable  $\delta$ -phase. When a tip of platinum wire once touched by a finger of the worker of the present experiment was brought in contact with the surface of the supercooled  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt or its  $\delta$ -phase during their cooling, they transformed into the stable  $\gamma$ -phase instantaneously. A trace of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  and  $\gamma$ - $\text{Bi}_2\text{O}_3$  crystals contaminating the sweat of the worker were concluded to be most probable nucleating agents for the formation of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ . These contaminants could not be removed completely from the skin of the worker by a simple washing with soap.

### I. INTRODUCTION

$6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  is a congruently melting composition with the equilibrium melting temperature of  $900^\circ\text{C}$ , below which it takes the  $\gamma$ -form as the stable phase.<sup>1,2)</sup> However, a thoroughly homogenized melt of this composition, when cooled naturally in a Pt crucible, does not precipitate the  $\gamma$ -phase but is supercooled to  $740^\circ\text{C}$ , where it precipitates only the metastable  $\delta$ -phase. The  $\delta$ -phase thus formed does not transform into the  $\gamma$ -phase from  $740^\circ\text{C}$  to room temperature.<sup>2,3)</sup> When an intensive mechanical shock is given to the supercooled melt or the  $\delta$ -phase during the cooling, they precipitates the  $\gamma$ -phase instantaneously.<sup>2,3)</sup>

The present authors recently found that the supercooled melt and the  $\delta$ -phase precipitate the  $\gamma$ -phase not only when they were given an intensive mechanical shock but also when their surface was chemically contaminated. For instance, they both transformed into the  $\gamma$ -phase instantaneously when a tip of platinum wire once touched by a finger of the worker engaged in the present experiment was brought in contact with their surfaces.

In this study, the mechanism of precipitation of the  $\gamma$ -phase induced by the surface contamination was investigated. Components of the contaminants, which acted as the nucleating agent for the formation of the  $\gamma$ -phase, were traced back to their origins.

### II. EXPERIMENT

#### 1. Contact with Platinum Wire

##### 1.1. Clean Platinum Wire

About 150 g of the batch mixture of the composition  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  was prepared

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from  $\text{Bi}_2\text{O}_3^*$  and  $\text{SiO}_2^*$  powders, both 99.99% pure. The batch mixture was charged into a Pt crucible of 50 ml, melted at  $1000^\circ\text{C}$  for 30 min in a SiC furnace, and then cooled at a rate of  $60^\circ\text{C}/\text{min}$ . During the cooling a tip of platinum wire 0.5 mm in diameter previously cleaned was brought in contact with the surface of the melt, at various temperatures  $880^\circ$  to  $740^\circ\text{C}$ , *i.e.* from the temperature just below the equilibrium melting temperature to that where the  $\delta$ -phase starts to precipitate spontaneously.<sup>2)</sup> The method for cleaning the Pt wire was as followed: The Pt wire was washed with a neutral soap, a distilled water, a concentrated HCl aqueous solution, and the distilled water, successively, and finally heated red with a town gas flame. The contact with the clean Pt wire caused no change in the melt.

The clean Pt wire was also brought in contact with the surface of the spontaneously precipitated  $\delta$ -phase during the cooling at various temperatures ranging from  $740^\circ\text{C}$  to room temperature. No change occurred also in the  $\delta$ -phase.

### 1.2. Naturally Contaminated Platinum Wire

When the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt was cooled to a temperature of  $880^\circ$ – $740^\circ\text{C}$ , a tip of the Pt wire once cleaned by the method described above and then touched by a finger of the worker of the present experiment was brought in contact with the surface of the melt. The crystallization of the melt commenced instantaneously from the contact point and proceeded rapidly and radially outwards, shining bright, as shown in Fig. 1(a). As soon as the crystallization of the whole melt was completed, the crucible was taken out from the furnace and quenched by dipping the bottom of the crucible into water. The crystals thus formed were identified as the stable  $\gamma$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  by a powder X-ray diffraction analysis.

The tip of the Pt wire touched by the human finger was also brought in contact with the surface of the spontaneously precipitated  $\delta$ -phase at a temperature of  $740^\circ$ – $550^\circ\text{C}$ . An exothermic reaction occurred with brightness from the contact point, and spread rapidly and radially outwards, as shown in Fig. 1(b). Crystals newly formed by this reaction were quenched and subjected to a powder X-ray diffraction analysis. They were identified as the  $\gamma$ -form of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ . The formation of the  $\gamma$ -form from

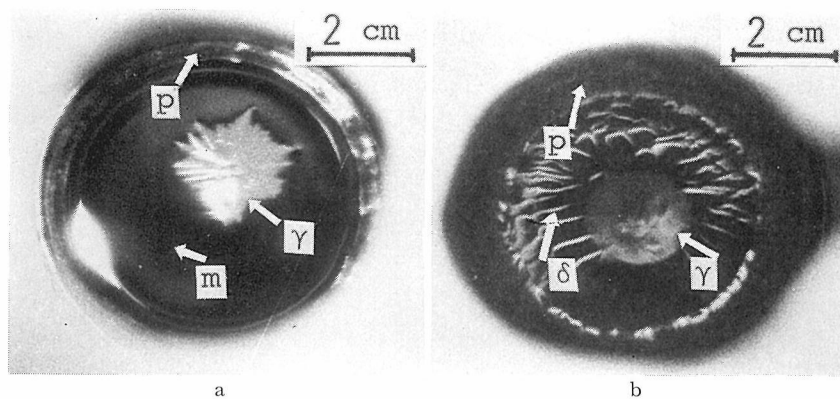


Fig. 1. Free surface of melt (a) and  $\delta$ -phase (b) in the middle of the precipitation of the  $\gamma$ -phase.  
m, melt;  $\gamma$ ,  $\gamma$ -phase;  $\delta$ ,  $\delta$ -phase; p, periphery of Pt crucible

\* Mitsuwa's Pure Chemicals Ltd., Osaka, Osaka-Fu.

the  $\delta$ -form did not occur when the  $\delta$ -phase was cooled to a temperature below 550°C.

Figure 2 shows optical micrographs of the  $\gamma$ -phases precipitated from the melt at 745°C and from the  $\delta$ -phase at 675°C, respectively. It can be seen from Fig. 2 that the  $\gamma$ -phases grew radially from the point of contact with the tip of the Pt wire. Figure 3 shows changes in length of the  $\gamma$ -phase crystals with time occurring in the melt at 745°C and in the  $\delta$ -phase at 675°C, respectively, each after the start of crystallization. These data were obtained from the photographs taken of the free surfaces of the melt and the  $\delta$ -phase at a rate of one frame per 0.5 seconds. In Fig. 3, change in length of the  $\delta$ -phase crystal with time, which precipitated spontaneously from the melt at 740°C,<sup>3)</sup> is also shown for comparison. The elongation rates of the  $\gamma$ -phase in the melt and in the  $\delta$ -phase determined from Fig. 3 were 3.7 and 5.1 mm/sec, respectively. They are much higher than that of the  $\delta$ -phase (0.14 mm/sec).

The formation of the  $\gamma$ -phase from the melt and the  $\delta$ -phase occurred even when the finger of the worker, which had previously been washed with soap, was brought in contact with these surfaces. In this case, however, the effect of inducing the formation of the  $\gamma$ -phase was a little weaker.

The formation of the  $\gamma$ -phase from the melt or the  $\delta$ -phase occurred also when the tip of the Pt wire previously touched by other parts of the body of the worker, by the

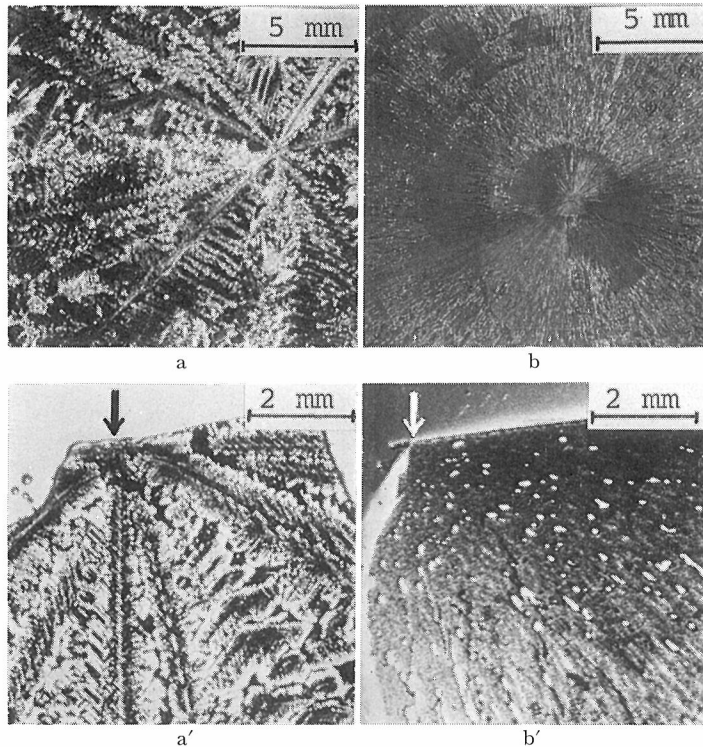


Fig. 2. Optical micrographs of  $\gamma$ -phase.  
 a ; free surface of  $\gamma$ -phase precipitated from melt at 745°C.  
 a' ; longitudinal section of  $\gamma$ -phase precipitated from melt at 745°C.  
 b ; free surface of  $\gamma$ -phase precipitated from  $\delta$ -phase at 675°C.  
 b' ; longitudinal section of  $\gamma$ -phase precipitated from  $\delta$ -phase at 675°C.  
 ↓ ; point where the specimen was brought in contact with Pt wire.

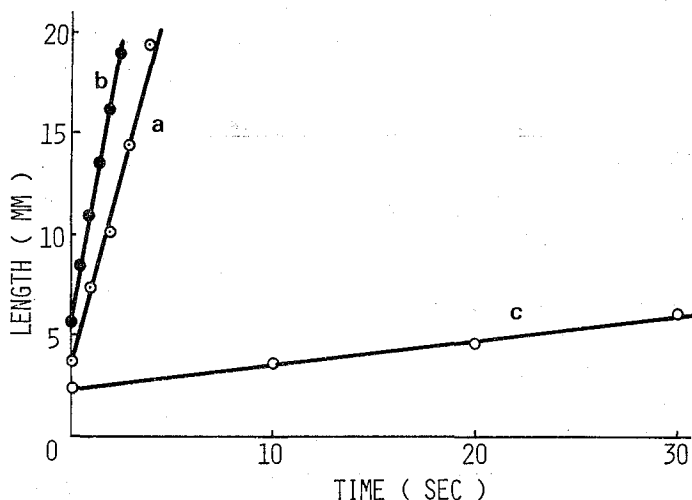


Fig. 3. Lengths of the  $\gamma$ -phase precipitated from the melt at  $745^\circ\text{C}$  (a) and from the  $\delta$ -phase at  $675^\circ\text{C}$  (b) and that of the  $\delta$ -phase precipitated from the melt at  $740^\circ\text{C}$  (c) as a function of time.

wall surfaces of the laboratory or by the surfaces of almost all of the articles such as desks and chairs placed for a long period in the laboratory. Furthermore, it occurred for the tip of the Pt wire previously touched by the body of the workers working in the rooms within a circle of about 30 m in diameter with the authors' laboratory for its center. It also occurred for the tip of the Pt wire touched by the surfaces of almost all of the articles placed in these neighboring rooms. In these cases, the effect of the contact of the Pt wire in inducing the formation of the  $\gamma$ -phase was weaker than that of the Pt wire previously touched by the finger of the worker of the present experiment. Generally, the effect of the contact lessened as the place of these workers and article, by that the Pt wire had been touched, is more distant from the laboratory. The Pt wire previously touched by a fresh surface of articles such as a newly fractured surface of the refractory brick had no effect of inducing the formation of the  $\gamma$ -phase.

## 2. Contact with Organic Materials

Various water and organic materials given in Table I, which generally exist on the skin of human body, were applied respectively, on the tip of the clean Pt wire described in section 1.1. The protein, fat, and saccharide were all reagent-grade chemicals.\* The blood, urine, and sweat were obtained from the worker of the present experiment. The sweat was extracted with distilled water from a piece of clean gauze applied on his breast after his vigorous exercise. The artificial sweat is an aqueous solution with the composition given in the foot note of Table I. It was prepared from reagent-grade chemicals\* of  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{NH}_4\text{OH}$ ,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , and distilled water. The human sweat is reported to contain a small amount of  $\text{C}_6\text{H}_{12}\text{O}_6$ , P, S,  $\text{SO}_4^{2-}$ , I, Cu, Mn, Fe, vitamine, hormone *etc*, in addition to the components described above.<sup>4)</sup> The tips of the Pt wire applied with each of these materials were brought in contact with the surfaces of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt at  $745^\circ\text{C}$

\* Nakarai Chemicals, Ltd., Kyoto, Kyoto-Fu.

Table I. Effects of Water and Organic Materials

Materials	Formation of $\gamma$ -phase	
	from melt	from $\delta$
Distilled water	×	×
Tap water	×	×
Protein (geratin, glysin, keratin or mixed amino acids*)	×	×
Fat (glycerin or stearic acid)	×	×
Saccharide (cellulose or saccharose)	×	×
Human blood	×	×
Human urine	×	×
Human sweat	○	○
Artificial sweat**	×	×

\* Amino acids calibration mixture for analysis.

\*\* Artificial sweat;  $\text{H}_2\text{O}$  99.38, Cl 0.34, Na 0.2, K 0.02, Ca 0.002, Mg 0.001, N in urea 0.015,  $\text{NH}_3$  0.005,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$  0.035 (wt%).

×: not occurred

○: occurred

and the  $\delta$ -phase at 675°C, respectively. Among the materials listed in Table I only the sweat obtained from the worker of the present experiment induced significantly the formation of the  $\gamma$ -phase both in the melt and the  $\delta$ -phase, as shown in Table I.

### 3. Contact with Inorganic Materials

Various inorganic materials given in Table II, which generally exist at least in minute amounts in chemical laboratories, were applied on the tips of the clean Pt wires and brought in contact with the surfaces of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt at 745°C and of its  $\delta$ -phase at 675°C, respectively. For all the inorganic materials tested no formation of the  $\gamma$ -phase from the melt and the  $\delta$ -phase was observed.

### 4. Contact with Bismuth Compounds

Bismuth compounds given in Table III were applied on the tips of the clean Pt wires and brought in contact with the surfaces of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt and its  $\delta$ -phase. The " $\delta$ - and  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ " crystals given in Table III were prepared by the methods

Table II. Effects of Inorganic Materials

Materials	Formation of $\gamma$ -phase	
	from melt	from $\delta$
Metal (Au, Ag, Cu, or Fe)	×	×
Simple substance (C or S)	×	×
Oxide ( $\text{B}_2\text{O}_3$ , $\text{Al}_2\text{O}_3$ , $\text{SiO}_2$ , $\text{P}_2\text{O}_5$ , CaO, $\text{MnO}_2$ , or $\text{PbO}$ )	×	×
Oxoacid Salt ( $\text{Li}_2\text{CO}_3$ , $\text{Na}_2\text{CO}_3$ , $\text{K}_2\text{CO}_3$ , $\text{NaHCO}_3$ , ( $\text{NH}_4$ ) $_2\text{CO}_3$ , $\text{CaSO}_4$ or $\text{Ca}(\text{NO}_3)_2$ )	×	×
Halogenide (NaCl, KCl, AgCl, KI, KBr, $\text{CaCl}_2$ , or $\text{MgCl}_2$ )	×	×

×: not occurred

# Formation of Stable $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ Crystal

Table III. Effects of Bismuth Compounds

Materials	Formation of $\gamma$ -phase	
	from melt	from $\delta$
$\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$	○	○
$\delta$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$	○	○
Vapor deposit of $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ ( $\delta$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ )	×	×
$\text{Bi}_2\text{O}_3$ as-supplied ( $\alpha$ - $\text{Bi}_2\text{O}_3$ )	○	○
$\text{Bi}_2\text{O}_3$ solidified after melted ( $\alpha$ - $\text{Bi}_2\text{O}_3$ )	×	×
$\text{Bi}_2\text{O}_2\cdot\text{CO}_3\cdot 1/2\text{H}_2\text{O}$ as-supplied	×	×
$\text{Bi}_2\text{O}_2\cdot\text{CO}_3\cdot 1/2\text{H}_2\text{O}$ heated		
at 300°C for 1 hr ( $\text{Bi}_2\text{O}_2\cdot\text{CO}_3$ )	●	×
// 400°C // ( $\beta$ - $\text{Bi}_2\text{O}_3$ )	○	○
// 500°C // ( $\alpha$ - $\text{Bi}_2\text{O}_3$ )	○	○
// 600°C // ( $\alpha$ - $\text{Bi}_2\text{O}_3$ )	○	○
// 700°C // ( $\gamma$ - $\text{Bi}_2\text{O}_3$ )	○	○

×: not occurred

○: occurred

●: sometimes occurred

( ): crystal identified by X-ray diffraction analysis

described in sections 1.1 and 1.2. The “Vapor deposit of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ ” was formed on a slide glass held at 5 cm distance above an opening of the furnace in which the melt was heated at 1350°C in the Pt crucible. The temperature of the slide glass, on which the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  was vapor-deposited, was about 100°C. The main component of the deposit was identified as the  $\delta$ -phase by an X-ray diffraction analysis. The “ $\text{Bi}_2\text{O}_3$  as-supplied” was a reagent-grade chemical\* commercially available and the “ $\text{Bi}_2\text{O}_3$  solidified after melted” is the same chemical but once melted on the tip of the Pt wire and then naturally solidified in air. Both the “ $\text{Bi}_2\text{O}_3$ ”s were identified as the  $\alpha$ - $\text{Bi}_2\text{O}_3$  crystal by an X-ray diffraction analysis. The “ $\text{Bi}_2\text{O}_2\cdot\text{CO}_3\cdot 1/2\text{H}_2\text{O}$  as-supplied” was also reagent-grade Chemical\* commercially available. The other “ $\text{Bi}_2\text{O}_2\cdot\text{CO}_3\cdot 1/2\text{H}_2\text{O}$ ” given in Table III were the same chemicals but once heated in clean Pt crucibles at the various temperatures indicated in Table III each for 1 hr and then quenched by dipping the bottom of the crucibles into water. The X-ray diffraction analyses showed that their main components were  $\text{Bi}_2\text{O}_2\cdot\text{CO}_3$ ,  $\beta$ -,  $\alpha$ - and  $\gamma$ - $\text{Bi}_2\text{O}_3$ , respectively, as shown in Table III.

Among the bismuth compounds, the “ $\delta$ - and  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ ”, the “ $\text{Bi}_2\text{O}_3$  as-supplied” and the “ $\text{Bi}_2\text{O}_2\cdot\text{CO}_3\cdot 1/2\text{H}_2\text{O}$  heated at the various temperatures above 400°C” effectively induced the formation of the  $\gamma$ -phase, when brought in contact with the surfaces of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt and its  $\delta$ -phase.

## 5. Contact with Sweat Subjected to Various Treatments

The sweat obtained from the worker (section 2.) was applied on the tip of the clean Pt wire described in section 1.1 and subjected to the various treatments indicated in Table IV, before it was brought in contact with the surface of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt or its  $\delta$ -phase.

\* Nakarai Chemicals, Ltd., Kyoto, Kyoto-Fu.

Table IV. Effects of Sweat Subjected to Various Treatments

Treatment	Formation of $\gamma$ -phase	
	from melt	from $\delta$
Heated at 125°C for 1 hr	○	○
// 400 //	○	○
// 500 //	○	●
// 600 //	●	×
// 700 //	●	×
// 800 //	×	×
Immersed in HCl aqueous solution of PH=1 for 5 min	×	×
// distilled water of PH=5 //	○	○
// NaOH aqueous solution of PH=13 //	○	○
Immersed in $\text{CHCl}_2\cdot\text{CH}_2\text{Cl}$ for 5 min	○	○
// $\text{C}_6\text{H}_6$ //	○	○
// $\text{CH}_3\text{COCH}_3$ //	○	○
// $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ //	○	○
// $\text{CCl}_4$ //	○	○

×: not occurred

●: occurred at intervals

○: occurred

The sweat subjected to the heat-treatment below 400°C preserved the effect of inducing the formation of the  $\gamma$ -phase in the melt and the  $\delta$ -phase. Its effect, however, diminished as the temperature of pretreatment was raised, and disappeared completely at 800°C. The sweat applied on the tip of the Pt wire preserved the effect of inducing the formation of the  $\gamma$ -phase even after it was immersed in a distilled water of PH=5, NaOH aqueous solution of PH=13 or various organic solvents given in Table IV each for 5 min, but it lost its effect after immersed in a HCl aqueous solution of PH=1 for 5 min.

The human sweat was evaporated to dryness in a clean Pt crucible and heated at the various temperatures indicated in Table IV for 1 hr. The X-ray diffraction patterns of the sweat did not change abruptly with temperature near 500°C.

#### 6. Contact with $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ Crystal Subjected to Various Treatments

The  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystal prepared by the method described in section 1.2 was powdered to -200 mesh *i.e.* into grain sizes smaller than  $74\ \mu\text{m}$  in diameter. The powder of 0.1 g was suspended in the artificial sweat of 100 ml. The powder alone and the suspension, *i.e.* the mixture of the powder and the artificial sweat, were applied each on the tip of the clean Pt wire, and brought in contact with the surface of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt at 745°C or with that of its  $\delta$ -phase at 675°C. In some cases, the powder or the suspension applied on the Pt wire was subjected to the various treatments indicated in Table V before being brought in contact with the surface of the melt or the  $\delta$ -phase. The results are given in Table V.

The powder alone and the suspension which were not subjected to any special treatments, effectively induced the formation of the  $\gamma$ -phase. After heat-treated at temperature above 700°C or immersed in the HCl aqueous solution of PH=1, however,



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Table V. Effects of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  and Its Suspension with Artificial Sweat Subjected to Various Treatments

Pre-treatment	Formation of $\gamma$ -phase			
	$\gamma$ -crystal		Suspension	
	from melt	from $\delta$	from melt	from $\delta$
No pre-treatment (as applied on the surface of Pt wire)	○	○	○	○
Heated at 125°C for 1 hr	○	○	○	○
// 400°C //	○	○	○	○
// 500°C //	○	○	○	○
// 700°C //	○	○	×	×
// 800°C //	○	○	×	×
Immersed in HCl aqueous solution of PH=1 for 5 min	○	○	×	×
// distilled water of PH=5 //	○	○	○	○
// NaOH aqueous solution of PH=13 //	○	○	○	○
Immersed in $\text{CHCl}_3\cdot\text{CH}_2\text{Cl}$ for 5 min	○	○	○	○
// $\text{C}_6\text{H}_6$ //	○	○	○	○
// $\text{CH}_3\text{COCH}_3$ //	○	○	○	○
// $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ //	○	○	○	○
// $\text{CCl}_4$ //	○	○	○	○

× : not occurred

○ : occurred

the suspension lost the effect of inducing the formation of the  $\gamma$ -phase, in a way similar to the human sweat described in section 5. The  $\gamma$ -phase powder alone, however, preserved its effect even after subjected to these treatments.

## III. DISCUSSION

The supercooled melt or the metastable  $\delta$ -phase of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  composition transformed into the stable  $\gamma$ -phase instantaneously, when the tip of the Pt wire once touched by the fingers of the worker engaged in the present experiment was brought in contact with their surfaces. The precipitation of the  $\gamma$ -phase commenced only from the point of the contact with the tip of the Pt wire and spread rapidly and radially, as shown in Figs. 1 to 3. These facts indicate that the contact with the tip of the Pt wire induces a heterogeneous nucleation of the  $\gamma$ -phase.

The nucleating agent, however, is not the Pt wire itself because the Pt wire previously cleaned by the procedure described in section 1 did not induce the formation of the  $\gamma$ -phase. The tips of the Pt wires once touched by the surfaces of the body of the worker or by the surfaces of almost all of the articles placed for a long period in the laboratory of the present experiment and also in its neighboring rooms were effective in inducing the formation of the  $\gamma$ -phase. These facts suggest that the nucleating agent must be some materials transferred to the surface of the tip of the Pt wire from the body of the worker or the articles described above.

The blood and urine of the worker of the present experiment were not effective in inducing the formation of the  $\gamma$ -phase. The proteins, fat and all components of the artificial sweat listed in Table I, which generally exist on the surface of the human body,

were also ineffective. These facts indicate that inorganic and organic materials freshly excreted from the human body can not be the nucleating agent for the formation of the  $\gamma$ -phase. The fact that the sweat of the worker of the present experiment strongly induced the formation of the  $\gamma$ -phase would be explained, if one considers that the sweat freshly secreted from the human body be contaminated easily with some materials falling, in the form of vapor or extremely fine solid particles, on the skin of the human body.

Among the materials arriving from outside at the surface of the skin, organic materials do not appear to act as the nucleating agent since the sweat obtained from the worker of the present experiment was found to preserve its effect even after heated at 400°C or immersed in the various organic solvents. The inorganic materials listed in Table II, which are likely to exist in ordinary chemical laboratories, however, were found experimentally ineffective.

The only inorganic materials which were confirmed to act as the nucleating agent for the formation of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  in its melt and  $\delta$ -phase were the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  and  $\gamma$ - $\text{Bi}_2\text{O}_3$  crystals. The latter has the structure identical to that of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  crystal.<sup>5)</sup> It is shown in Table III that beside these two compounds the other three, *i.e.*, the " $\delta$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ " prepared by cooling its melt in the Pt crucible, the " $\text{Bi}_2\text{O}_3$  as-supplied ( $\alpha$ - $\text{Bi}_2\text{O}_3$ )" and the " $\text{Bi}_2\text{O}_3\cdot\text{CO}_3\cdot 1/2\text{H}_2\text{O}$  heated at a temperature of 400°–700°C", also induced the formation of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ . It was reported elsewhere<sup>8)</sup> that the " $\delta$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ " crystals prepared by cooling its melt gently down to room temperature in a Pt crucible transformed into the  $\gamma$ -phase at about 500°C on its reheating due to residual thermal stresses accumulated in the crystals. Therefore, the " $\delta$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ " powder applied on the tip of the Pt wire must have transformed into the  $\gamma$ -phase just before the tip of the Pt wire was brought in contact with the surface of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt or its  $\delta$ -phase. Therefore, in this case, the  $\gamma$ -phase thus formed actually acted as the nucleating agent. The "vapor deposit of  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ " on the slide glass can not be transformed into the  $\gamma$ -phase by reheating, since thermal stresses strong enough to cause the transformation can not be accumulated in its thin film. The " $\text{Bi}_2\text{O}_3$  as-supplied" was mainly composed of the  $\alpha$ - $\text{Bi}_2\text{O}_3$ . The  $\alpha$ - $\text{Bi}_2\text{O}_3$  itself, however, does not act as the nucleating agent for the formation of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ , since the  $\alpha$ - $\text{Bi}_2\text{O}_3$  prepared by melting the " $\text{Bi}_2\text{O}_3$  as-supplied" for its homogenization had no effect of inducing the formation of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ . Nucleating agent in the " $\text{Bi}_2\text{O}_3$  as-supplied" is probably the  $\gamma$ - $\text{Bi}_2\text{O}_3$  having the structure identical to that of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  which coexist in a trace with the  $\alpha$ - $\text{Bi}_2\text{O}_3$  in the " $\text{Bi}_2\text{O}_3$  as-supplied". It is natural that the  $\gamma$ - $\text{Bi}_2\text{O}_3$  obtained by heating the  $\text{Bi}_2\text{O}_3\cdot\text{CO}_3\cdot 1/2\text{H}_2\text{O}$  at 700°C was effective in inducing the formation of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  (Table III) since the crystal structure of the former is identical to that of the latter as described above. The facts that the materials obtained by heating the  $\text{Bi}_2\text{O}_3\cdot\text{CO}_3\cdot 1/2\text{H}_2\text{O}$  at 400°, 500°, and 600°C, respectively, were also effective would indicate that, although they were identified as the  $\beta$ - or  $\alpha$ - $\text{Bi}_2\text{O}_3$  by X-ray diffraction analyses, they both contained a trace of the  $\gamma$ - $\text{Bi}_2\text{O}_3$ .

There are four possible sources of the  $\gamma$ - $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  and  $\gamma$ - $\text{Bi}_2\text{O}_3$  : 1) The  $\gamma$ - $\text{Bi}_2\text{O}_3$  originally contained in a trace in the  $\text{Bi}_2\text{O}_3$  chemical as-supplied was scattered in the process of preparation of the  $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$  melt and caught by the sweat of the worker

engaged in the present experiment. 2) The  $\alpha$ - $\text{Bi}_2\text{O}_3$  which is the main component of the " $\text{Bi}_2\text{O}_3$  as-supplied" was scattered in the same process as described in 1), and transformed into the  $\gamma$ - $\text{Bi}_2\text{O}_3$  by some mechanism, *e.g.*, via formation of the  $\text{Bi}_2\text{O}_2 \cdot \text{CO}_2 \cdot 1/2\text{H}_2\text{O}$ , before or after caught by the sweat. 3) The  $\gamma$ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  crystals formed from its melt or the  $\delta$ -phase in the present experiment were scattered and caught by the sweat. 4) The  $\delta$ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  crystals formed from its melt as the vapor deposit transformed into the  $\gamma$ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  by some catalysis or stress accumulation *etc.* before or after caught by the sweat: The  $\gamma$ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  and  $\gamma$ - $\text{Bi}_2\text{O}_3$  may be caught not only by the skin of the worker of the present experiments but also by the surfaces of the articles present in the laboratory or in its neighborhood. The contaminants once mixed with or dissolved into the sweat would strongly adhere to the surface of the human skin and hardly be removed from the skin completely by simple washing with soap. In some cases, a part of these contaminants in the sweat may be communicated by contact from the skin of the workers to the surfaces of the articles placed for a long period in the laboratory and its neighboring rooms.

It was described in section 6 that the  $\gamma$ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  powder suspended in the artificial sweat showed a very similar behavior to that of the human sweat; *i.e.*, the suspension and the human sweat both induced the formation of the  $\gamma$ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$ , even after heated at  $400^\circ$ – $500^\circ\text{C}$  or immersed in the  $\text{NaOH}$  solution of  $\text{pH}=13$ , but not after heated above  $700^\circ\text{C}$  or immersed in the  $\text{HCl}$  solution of  $\text{pH}=1$ . This supports the authors' conclusion that a trace of  $\gamma$ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  or  $\gamma$ - $\text{Bi}_2\text{O}_3$  contaminating the sweat of the worker acts as the nucleating agent for the formation of the  $\gamma$ - $6\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$  in its melt and  $\delta$ -phase.

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